Crystal Orientation of Spinel Type Ferrite during Solid-Solid Reaction (Commemoration Issue Dedicated to Professor Tsunenobu Shigematsu on the Occasion of his Retirement)

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Bull. Inst. Chem. Res., Kyoto Univ., Vol. 58, No. 2, 1980

Crystal Orientation of Spinel Type Ferrite during Solid-Solid Reaction

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Received March 11, 1980

The formation from hydroxides and iron oxyhydroxides to spinel type ferrites by solid state reaction was studied by electron microsopy and X-ray diffraction. The ferrite formation proceeded topotaxially and the crystallographic orientation relationships among the oxyhydroxide, oxide and spinel type ferrite were as follows.

(100) [001] α-FeOOH // (0001) [$\bar{1}$100] α-Fe_2O_3 // (111)[$\bar{1}$01] MFe_2O_4 (M: Mg, Mn, Co, Ni and Zn)

(100) [001] γ-MnOOH // (111) [101] $MnFe_2O_4$

(100) [001] γ-FeOOH // (110) [1$\bar{1}$0] MFe_2O_4 (M: Mn, Co and Ni)

Particles of α-FeOOH, γ-FeOOH, γ-MnOOH and metal hydroxides showed preferential orientations of [100], [100], [100] and [0001] axis by uniaxial pressing, respectively.

The [111] or [110] axis oriented ferrites were directly obtained by heating the mixture of α-FeOOH or γ-FeOOH and metal hydroxides.

KEY WORDS : Topotaxy / Spinel ferrite / Crystal orientation / Uniaxially oriented ferrite/

INTRODUCTION

In many reactions involving a solid, it has been observed that a single crystal of starting material is converted into a single crystal of the product, and there exists a definite three dimensional crystal orientation relationship between the respective lattices. The term "topotaxy" has been used to describe these reactions. Studies on topotaxy have been mainly made on the decomposition of a single crystal or on the reaction of a single crystal with a gas phase.

It is well known that there are two modifications, α- and γ-forms, in FeOOH. Oxygen ions in α-FeOOH (orthorhombic: a=4.64A, b=10.0A, c=3.03A) are hexagonally closed packed and in γ-FeOOH (orthorhombic: a=12.50A, b=3.86A, c=3.06A) cubically closed packed. By heating, α-FeOOH transformed to α-Fe_2O_3 and γ-FeOOH to γ-Fe_2O_3. The arrangement of oxygen layers is conserved during transformation.

The α-Fe_2O_3 to Fe_3O_4 transformation accompanies with change from AB oxygen stacking to ABC stacking. In this transformation, (0001) plane of α-Fe_2O_3 is parallel to (111) plane of Fe_3O_4. The same relationships may be expected in the spinel ferrite

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formation between α-Fe_2O_3 and a metal oxide.

The mechanism of the solid state reaction between MO (M: Co, Ni, Mg and Zn) and A_2O_3 (A: Al and Fe) to form spinel type crystal MA_2O_4 has been studied using single crystals by many investigators.[1-3]

They concluded that the MA_2O_4 formed by the counter diffusion of A and M cations through the rigid oxide lattice. The crystallographic relation between Al_2O_3 and $MgAl_2O_4$ was determined as (0001) [1010] Al_2O_3//(111) [110] $MgAl_2O_4$.[2]

In the present report, the investigation on topotaxy was made on the formation of manganese, cobalt, nickel, magnesium and zinc ferrite using hydroxides and oxyhydroxides.

At first, the topotaxy on spinel ferrite formation is examined using electron microscope. Secondary, the topotaxy is also examined by some experiments with oriented particles of metal hydroxides, and iron and manganese oxyhydroxides. The experiment of this type using oriented particles of α-FeOOH had been carried out on formation of $SrO \cdot 6Fe_2O_3$.[4]

EXPERIMENTALS

1. Starting materials

Fine particles of α-FeOOH, γ-FeOOH, γ-MnOOH, $Ni(OH)_2$, $Co(OH)_2$ and $Mg(OH)_2$ as shown in Fig, 1 were used as starting materials. Granular particles of α-Fe_2O_3, Mn_3O_4, NiO, CoO, MgO and ZnO were also used.

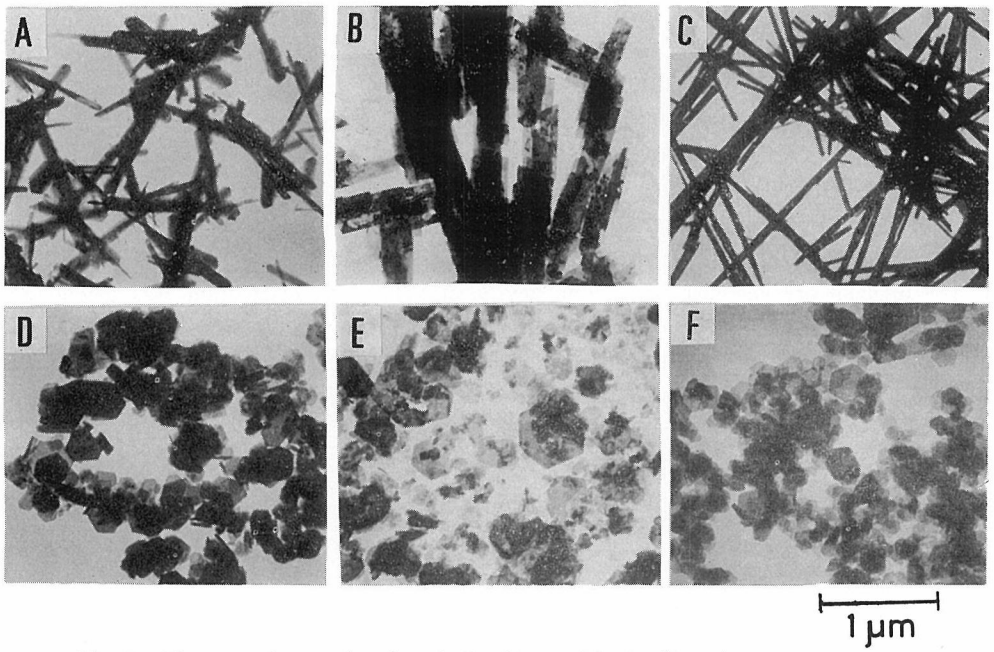

Fig. 1. Electron micrographs of oxyhydroxides and hydroxides, (A) α-FeOOH, (B) γ-FeOOH, (C)γ-MnOOH, (D) $Mg(OH)_2$, (E) $Ni(OH)_2$ and (F) $Co(OH)_2$.

2. Microscopic examination

The particles shapes and crystal orientations of starting materials were examined

using electron microscope. Particles of α-FeOOH are needles elongated parallel to [001] and its dendrite is used to determine the crystal orientation. Particles of γ-FeOOH are lamella with (100) plane and elongate parallel to [001]. Particles of γ-MnOOH (pscudoorthorhombic: a=8.98A, b=5.28A, c=5.71A) are very long needles elongated to [001].

The mixture of α-FeOOH and a metal hydroxide was heated at low temperatures from 600°C to 800°C to keep the original shape of needle unchanged. The particles of ferrite obtained were also examined by electron microscopy and diffraction. Orientation relations were determined in consideration of the shape of particle.

3. Experiments using oriented particles

Starting materials of hydroxides and oxyhydroxides were uniaxially pressed. X-ray diffractions using Fe-K_α radiation were taken on the surfaces parallel and perpendicular to the direction of the uniaxial pressing to determine the orientation of particles.

The degree of particle orientation in α-FeOOH compact was estimated from the X-ray diffraction patterns of α-Fe_2O_3 compact obtained by heating α-FeOOH compact at 400°C. As the α-FeOOH to α-Fe_2O_3 transformation is (100) α-FeOOH// (0001) α-Fe_2O_3, the [100] orientation of α-FeOOH particles in the compact should lead to the [0001] orientation of α-Fe_2O_3 particles. The diffraction patterns from the plane perpendicular to the hexagonal axis [0001] of α-Fe_2O_3 appeared intensified on the surface perpendicular to the direction of pressing. Therefore, it was concluded that the α-FeOOH particles were oriented to [100] direction by uniaxial pressing.

In case of $Ni(OH)_2$, $Co(OH)_2$ and $Mg(OH)_2$, X-ray diffraction patterns from the plane perpendicular to the hexagonal axis [0001] appeared much intensified, when patterns were obtained on the surface perpendicular to the direction of pressing.

The mixtures of α-FeOOH and metal hydroxide with mole ratio Fe/M equal to 2 were uniaxially pressed by wet method and the orientation of particles was examined by X-ray diffraction. The specimens were heated at temperatures ranging from 1100°C to 1300°C for 2 to 24 hrs in air or nitrogen atmosphere. The orientation of the polycrystalline ferrites obtained was also examined on polished surfaces parallel and perpendicular to the uniaxial pressing direction. The degree of [111] axis orientation was calculated from the intensities I of X-ray diffraction patterns and orientation factor f is defined by $f(111)=(P-Pr)/(1-Pr)$, where $P=\sum I(111)/I(hkl)$ for the oriented specimens and Pr for the randomly oriented specimen. As P varies from Pr to 1, f varies between 0 (non orientation) and 1 (complete orientation).[5,6]

RESULTS

1. Microscopic Examination

a) Formation of spinel ferrite from α-FeOOH When the mixture of α-FeOOH and $Ni(OH)_2$ was heated in air, these particles transformed to the respective oxides and finally to the nickel ferrite. $2FeOOH+Ni(OH)_2 \rightarrow \alpha\text{-}Fe_2O_3+NiO \rightarrow NiFe_2O_4$. The particle shape of α-Fe_2O_3 obtained by decomposition of α-FeOOH below 800°C was also very close to that of α-FeOOH, as shown in Fig. 2-(A). The particle shape of ferrite prepared by heating the mixture below 800°C was also close to that of α-FeOOH, as

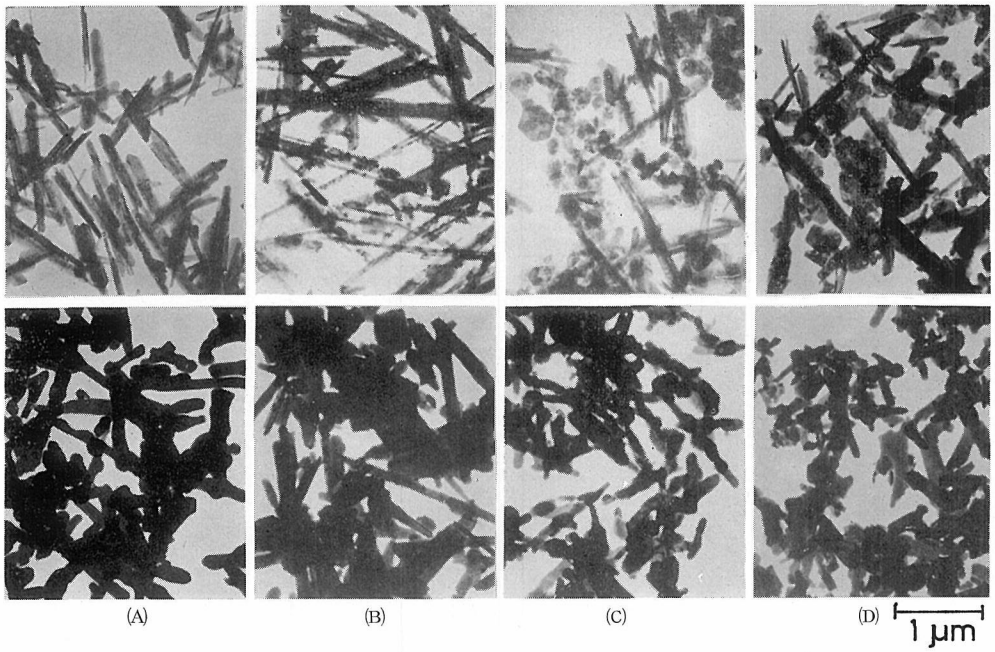

Fig. 2. Electron micrographs of mixed starting materials (upper photograph) and particles obtained by heating at 800°C (lower photograph) (A) α-FeOOH $\rightarrow\alpha$-Fe_2O_3, (B) 2α-FeOOH+γ-MnOOH$\rightarrow$$MnFe_2O_4$, (C) 2$\alpha$-FeOOH+Co-$(OH)_2\rightarrow$$CoFe_2O_4$ and (D) 2α-FeOOH+$Ni(OH)_2\rightarrow$$NiFe_2O_4$.

shown in Fig. 2-(B, C and D).

Crystallographic examination using the electron microscope was made on the thin plate like particles. We could easily find the same plane of product as that of α-FeOOH. Electron micrographs, electron diffraction patterns and the corresponding dark field images of α-FeOOH, α-Fe_2O_3 and ferrite particles were shown in Fig. 3. It is clear that a product particle is a single crystal or a aggregate consisting of highly oriented crystallites.

The incident direction of the electron beam is parallel to [100] direction for α-FeOOH and [111] direction for ferrite. The direction of the longitudinal axis of the thin plate was determined from analysis of the dark field image. Crystal orientation of plates of α-FeOOH, α-Fe_2O_3 and ferrite are shown schematically in Fig. 4. The orientation relationship was the same in formation of $CoFe_2O_4$, $MgFe_2O_4$, $ZnFe_2O_4$ and $MnFe_2O_4$.

b) Formation of spinel ferrites from metal hydroxides Ferrite particles which conserved the hexagonal shape of $Ni(OH)_2$, $Co(OH)_2$ and $Mg(OH)_2$ were not observed. Therefore, the orientation relationship between the hydroxide and the ferrite could not be determined.

c) Formation of manganese ferrite from γ-MnOOH In manganese ferrite formation, the orientation relationship between γ-MnOOH and manganese ferrite was determined using needle like particles of γ-MnOOH and granular particles of α-Fe_2O_3($>0.1\mu$). The mixture was heated at 800°C in nitrogen atmosphere. The particle shape of manganese ferrite obtained was close to that of γ-MnOOH. The orientation relation: (100) [001] γ-MnOOH// (111) [101] $MnFe_2O_4$ was obtained from analysis of electron microscopic observation, as shown in Fig. 5

The mixture of γ-MnOOH and α-Fe_2O_3 changed as follows: γ-MnOOH+δ-Fe_2O_3

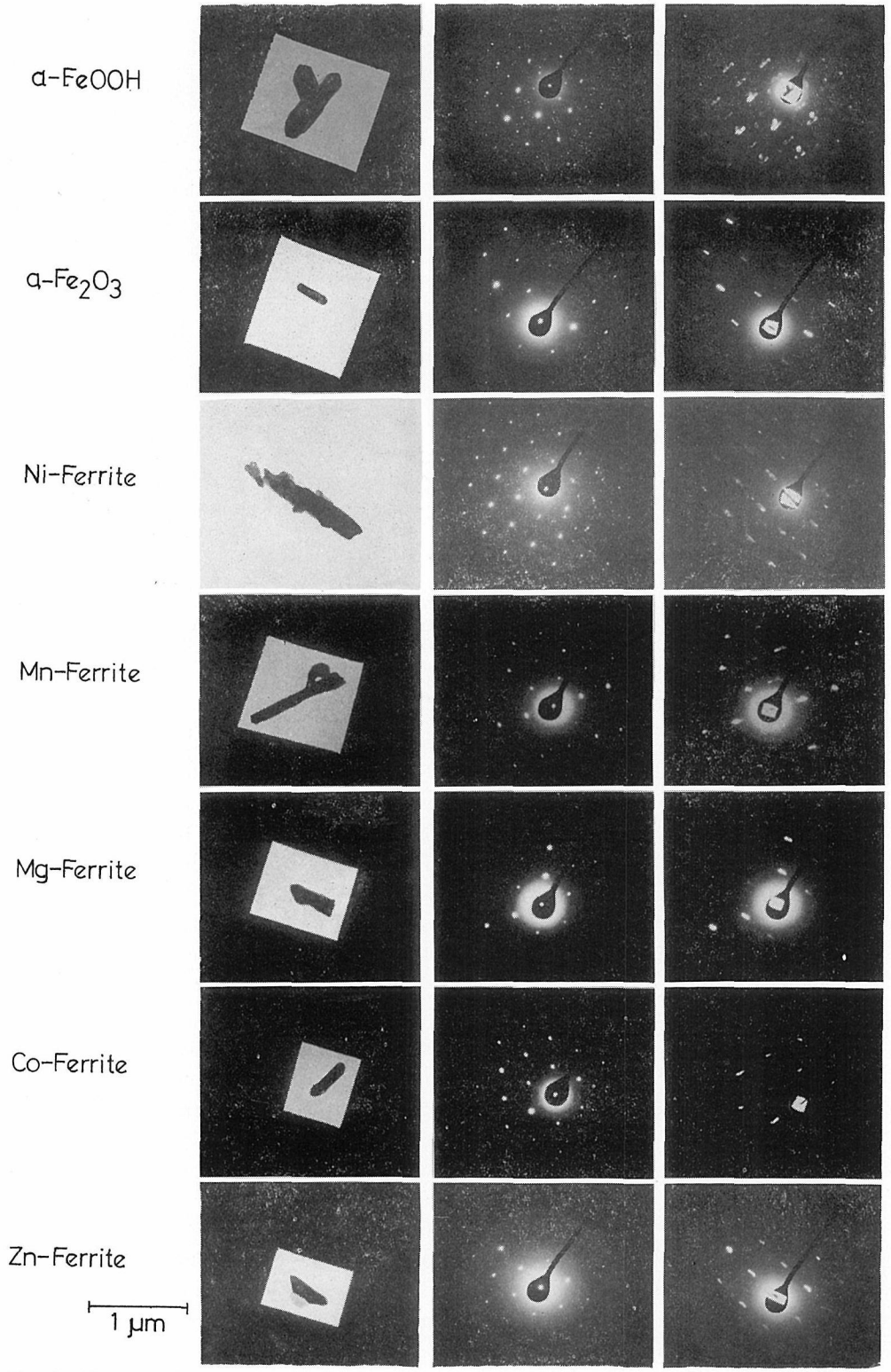

Fig. 3. Electron micrographs, electron diffraction patterns and the corresponding dark field images

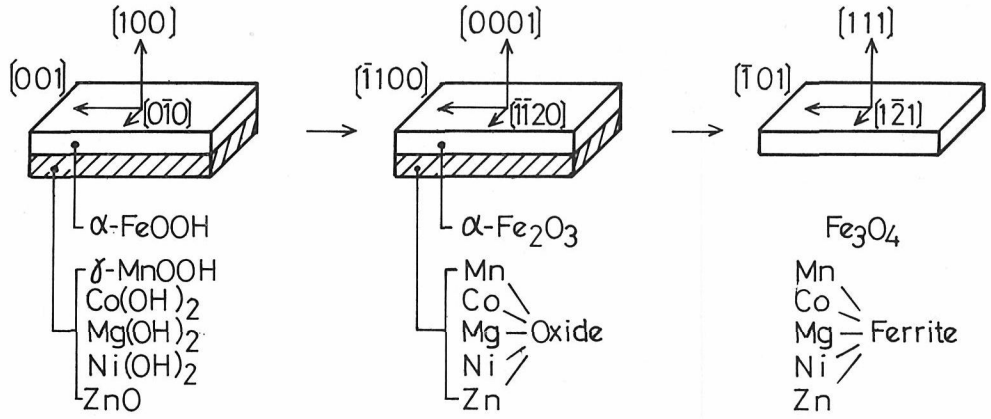

Fig. 4. Illustration on the crystal orientations of plates of α-FeOOH, α-Fe_2O_3 and the ferrite.

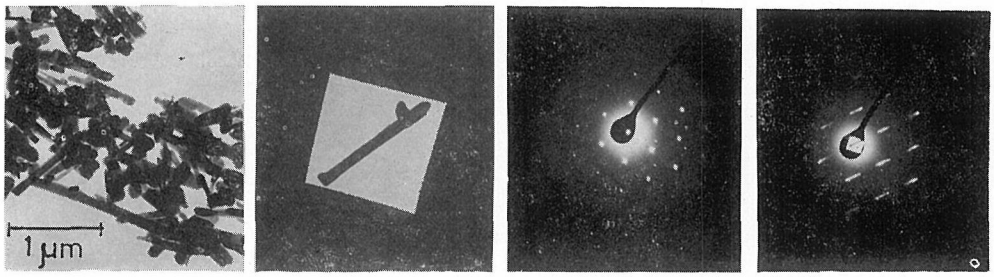

Fig. 5. Manganese ferrite particles obtained by heating the mixture (α-Fe_2O_3+γ-MnOOH) at 800°C (A) and (B) electron micrographs (C) electron diffraction pattern and (D) the corresponding dark field image.

$\xrightarrow{400°C}$ $Mn_5O_8+\alpha$-Fe_2O_3 $\xrightarrow{600°C}$ $Mn_3O_4+\alpha$-Fe_2O_3 $\xrightarrow{700°C}$ $MnFe_2O_4$. The transformation of the series γ-MnOOH-Mn_5O_8 and Mn_5O_8-Mn_3O_4 have been reported to proceed in an oriented fashion.[7] The orientation between γ-MnOOH and Mn_3O_4 is (100) [001] γ-MnOOH// (101) [010] Mn_3O_4. The relationships between Mn_3O_4 and spinel ferrite are expected to be (101) [010] Mn_3O_4// (111) [110] $MnFe_2O_4$. The (101) plane of Mn_3O_4 corresponds to close packed oxygen plane.

d) Formation of spinel ferrite from γ-FeOOH Change of the mixture of γ-FeOOH and $Ni(OH)_2$ by heating in air was as follows: 2γ-FeOOH+$Ni(OH)_2$ $\xrightarrow{300°C}$ γ-Fe_2O_3+

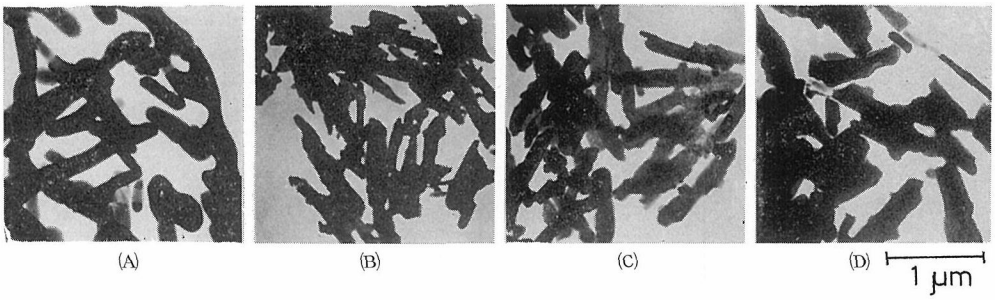

Fig. 6. Electron micrographs of particles obtained by heating the mixtures at 800°C, (A) α-Fe_2O_3, (B) Ni-ferrite, (C) Co-ferrite and (D) Mn-ferrite.

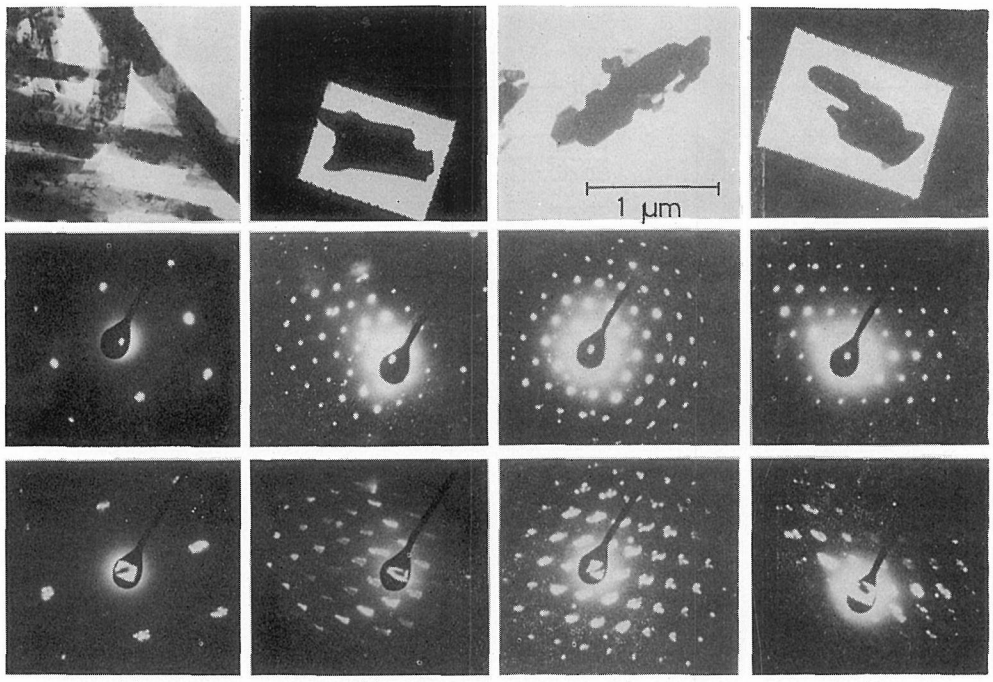

Fig. 7. Electron micrographs, electron diffraction patterns and the corresponding dark field images, (A) γ-FeOOH, (B) Ni-ferrite. (C) Mn-ferrite and (D) Co-ferrite.

$NiO \xrightarrow{500°C} \alpha\text{-}Fe_2O_3 + NiO \xrightarrow{700°C} NiFe_2O_4$.

As shown in Fig. 6, the particle shape of spinel ferrite obtained was close to that of γ-FeOOH. The (100) plane of γ-FeOOH was parallel to (110) plane of nickel ferrite and [001] of γ-FeOOH to [110] of spinel ferrite from analysis of electron diffraction in Fig. 7. The orientation relations among γ-FeOOH, γ-Fe_2O_3 and α-Fe_2O_3 has been reported to be (100) [001] γ-FeOOH // (110) [110] γ-Fe_2O_3 and (111) [110] γ-Fe_2O_3 // (0001) [0110] α-Fe_2O_3.[8-11] Therefore, the orientation relation between α-Fe_2O_3 and spinel ferrite was the same, independently of kind of iron oxyhydroxides (α-or γ-FeOOH).

2. Orientation of Starting Materials and Formation of spinel Ferrite

When [100] of α-FeOOH particles is oriented in the mixture, it is expected from the above mentioned relation that [111] of spinel ferrite crystallites would orient preferentially. By uniaxial pressing, α-, γ-FeOOH and γ-MnOOH particles showed orientation of [100]. Thin hexagonal platelets such as $Co(OH)_2$, $Ni(OH)_2$ and $Mg(OH)_2$ particles preferentially oriented parallel to [0001] axis. Oxide granular particles ($>0.5\mu$) of α-Fe_2O_3, Mn_3O_4, Co_3O_4, NiO, MgO and ZnO were not oriented by uniaxial pressing. The degree of orientation depended greatly on shape and size of the particles. Particularly, dendrite of α-FeOOH showed good orientation.

Experimental results for orientation of ferrite obtained from various mixtures were shown in Table I.

$MnFe_2O_4$ The samples were fired for 24 hrs at 1200°C in nitrogen atmosphere. The ferrites contained no trace of second phase. The X-ray diagram of the best ori-

Table I. Orientation of the starting materials and degree of ⟨111⟩ orientation of the ferrites.

Compound	Starting material and direction of orientation			Degree of ⟨111⟩ orientation (f)	
$MnFe_2O_4$: M-A	α-FeOOH [100]	γ-MnOOH	[100]	Very good	(f=1)
$MnFe_2O_4$: M-B	α-FeOOH [100]	Mn_3O_4		Good	(f=0.5)
$MnFe_2O_4$: M-C	α-Fe_2O_3	γ-MnOOH	[100]	Moderate	(f=0.3)
$MnFe_2O_4$: M-D	α-Fe_2O_3	Mn_3O_4		Non	(f=0)
$CoFe_2O_4$: C-A	α-FeOOH [100]	β-$Co(OH)_2$	[0001]	Very good	(f=0.8)
$CoFe_2O_4$: C-B	α-FeOOH [100]	Co_3O_4		Moderate	(f=0.3)
$CoFe_2O_4$: C-C	α-Fe_2O_3	β-$Co(OH)_2$	[0001]	Poor	(f=0.1)
$CoFe_2O_4$: C-D	α-Fe_2O_3	Co_3O_4		Non	(f=0)
$NiFe_2O_4$: N-A	α-FeOOH [100]	$Ni(OH)_2$	[0001]	Very good	(f=0.7)
$NiFe_2O_4$: N-B	α-FeOOH [100]	NiO		Moderate	(f=0.3)
$NiFe_2O_4$: N-C	α-Fe_2O_3	$Ni(OH)_2$	[0001]	Poor	(f=0.1)
$NiFe_2O_4$: N-D	α-Fe_2O_3	NiO		Non	(f=0)
$MgFe_2O_4$: G-A	α-FeOOH [100]	$Mg(OH)_2$	[0001]	Very good	(f=0.8)
$MgFe_2O_4$: G-B	α-FeOOH [100]	MgO		Moderate	(f=0.3)
$MgFe_2O_4$: G-C	α-Fe_2O_3	$Mg(OH)_2$	[0001]	Poor	(f=0.1)
$MgFe_2O_4$: G-D	α-Fe_2O_3	MgO		Non	(f=0)
$ZnFe_2O_4$: Z-B	α-FeOOH [100]	ZnO		Poor	(f=0.2)

ented sample M-A is given in Fig. 8, and shows the complete [111] orientation of $MnFe_2O_4$ crystallite.

The samples M-B and M-C were less oriented than the sample M-A. These facts support that [100] orientation of α-FeOOH and γ-MnOOH lead to [111] orientation of manganese ferrite. The fact that the orientation of α-FeOOH as well as γ-MnOOH in the initial mixture increased the degree of [111] orientation of manganese ferrite con-

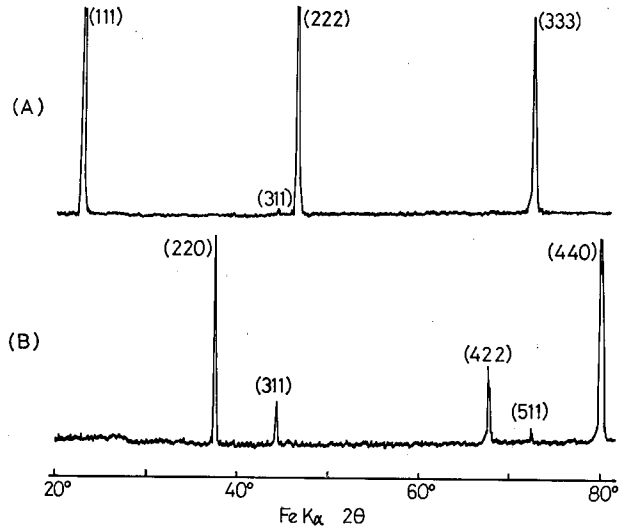

Fig. 8. X-ray diffraction patterns of the manganese ferrite on the surfaces perpendicular (A) and parallel (B) to uniaxial pressing direction.

firmed for the transformations from α-Fe_2O_3 to manganese ferrite and from Mn_3O_4 to manganese ferrite to be topotactic, as was concluded from the electron microscopic examination.

$NiFe_2O_4$, $CoFe_2O_4$ and $MgFe_2O_4$ The samples were fired for 24 hrs at 1200°C in air. The obtained ferrites contained no trace of second phase. The use of α-FeOOH or metal hydroxide as starting materials gave the ferrite crystallite the [111] orientation to some degree. The mixture of α-FeOOH and metal hydroxide gave the best oriented samples. The amount of oriented component in the initial mixture was the determining factor in the orientation of final product. This fact suggests the transformations from NiO, Co_3O_4 and MgO to $NiFe_2O_4$, $CoFe_2O_4$ and $MgFe_2O_4$, respectively are topotactic as following.

$Co(OH)_2$ ····· Co_3O_4····· $CoFe_2O_4$
$Ni(OH)_2$ ····· NiO ····· $NiFe_2O_4$
$Mg(OH)_2$····· MgO ····· $MgFe_2O_4$
(0001) // (111) // (111)

Orientation relations of the hydroxides to oxides transformation had already determined using electron microscope.[12,13]

[110] oriented ferrite The [110] oriented ferrites were obtained from the mixture containing γ-FeOOH particles, but the degree of their orientation was not so good as that of [111] orientation of the ferrite obtained from α-FeOOH, because the orientation of starting materials such as γ-MnOOH, $Ni(OH)_2$ and $Co(OH)_2$ produced [111] oriented ferrite.

The present investigation proposed the new method for the preparation of polycrystalline ferrites with [111] oriented crystals, as reported by Bando et al.[14]

ACKNOWLEDGMENT

The authors would like to thank to M. Kiyama and K. Tabaru for their helps in the metal hydroxide preparation.

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